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COMPOSITES CONTAINING BARRIER LAYERS FOR REDUCED PERMEABILITY AT CRYOGENIC TEMPERATURES (PREPRINT)

Vernon T. Bechel, Steven L. Donaldson, and Ran Y. Kim

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14. ABSTRACT
To help prevent leakage that may occur if cracks develop in a cryogenic composite pressure vessel due to thermo-mechanical fatigue, liners are occasionally implemented. However, liners can be difficult to fabricate and maintain, and mismatch of their CTE with the underlying composite can promote debonding of the liner. In this effort two approaches to incorporating a barrier layer directly into a carbon/bismaleimide PMC (IM7/5250-4) were investigated for their effectiveness in preventing the development of through-thickness crack networks that can lead to leakage. In the first concept, a "thin ply" of T800 carbon fiber/5250-4 bismaleimide composite much thinner than a standard 0.13 mm thick ply was placed adjacent to the surface plies or mid-plane ply group where cracks initiated first. This arrangement was chosen to help prevent crack growth beyond these early-cracking plies. Overall the thin plies were successful both in limiting "stitch crack" propagation into the neighboring plies and in limiting the overall interior ply damage. In the second concept, an even thinner layer (<0.25 mm thick) of electro-spun PAN fibers infused with 5250-4 was again placed next to the surface plies. The electro-spun fiber layer did not prevent crack growth from the surface plies into the neighboring plies but did significantly limit the interior ply damage that formed.

15. SUBJECT TERMS
Cryogenic composite pressure vessel, carbon/bismaleimide PMC (IM7/5250-4), ply, crack growth

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Composites Containing Barrier Layers for Reduced Permeability at Cryogenic Temperature

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To help prevent leakage that may occur if cracks develop in a cryogenic composite pressure vessel due to thermo-mechanical fatigue, liners are occasionally implemented. However, liners can be difficult to fabricate and maintain, and mismatch of their CTE with the underlying composite can promote debonding of the liner. In this effort two approaches to incorporating a barrier layer directly into a carbon / bismaleimide PMC (IM7 / 5250-4) were investigated for their effectiveness in preventing the development of through-thickness crack networks that can lead to leakage. In the first concept, a "thin ply" of T800 carbon fiber / 5250-4 bismaleimide composite much thinner than a standard 0.13 mm thick ply was placed adjacent to the surface plies or mid-plane ply group where cracks initiated first. This arrangement was chosen to help prevent crack growth beyond these early-cracking plies. Overall the thin plies were successful both in limiting "stitch crack" propagation into the neighboring plies and in limiting the overall interior ply damage. In the second concept, an even thinner layer (< 0.025 mm thick) of electro-spun PAN fibers infused with 5250-4 was again placed next to the surface plies. The electro-spun fiber layer did not prevent crack growth from the surface plies into the neighboring plies but did significantly limit the interior ply damage that formed.

I. Introduction

Various studies have detailed the potentially leakage inducing damage that can accumulate in polymer matrix composites (PMCs) when subject to thermal cyclic loading that includes extremely low temperatures. The severity of this damage depends on many things including the mechanical and CTE properties of the composite plies, the profile of the thermal cycle, whether mechanical cycling is included, and the number of cycles applied.[1-3] However, a few recent research efforts and tests of prototype components indicate that the permeability of at least a few carbon / epoxy composites can be reasonably controlled through appropriate lay-up, material choice, and loading considerations. These studies are preliminary evidence that it is possible to safely and effectively use composites to reduce the weight and cost of various cryogenic launch components such as cryogenic fuel tanks.

On the other hand, the challenges in the implementation of polymer matrix composites continue. The implementation of a wider range of composites with characteristics beyond those of medium service temperature autoclave cured composites such as the carbon / epoxies referred to above can bring new capabilities to these structures. For example, the use of higher temperature PMCs in these components may be advantageous because the vehicle could be designed with less thermal protection or possibly with a lower temperature, lower cost, or lower maintenance thermal protection system. Low-temperature-cured PMCs, out-of-autoclave processed PMCs, or carbon nano-tube modified multi-functional PMCs may be desired for these cryogenic components to reduce fabrication costs or add functionality to the structure such as being part of an energy harvesting or energy storage system. PMCs with improved LOX impact resistance are also being sought. As a trade-off for improved LOX compatibility these materials may have reduced leakage resistance as compared to the best current carbon / epoxy composites. Each of these new composites presents unique difficulties when considering how to control permeability. Researchers are already studying the issues related to the use of high temperature PMCs[4-5] and low temperature cured PMCs[6] in cryo-cyclic environments. So while this area has received considerable attention in the last five years and great progress has been made, new approaches will likely be needed to realize the advantages of these emerging classes of PMCs in cryogenic cyclic applications.

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Polymer or even metal liners have on occasion been used in cryogenic composite pressure vessels as a primary or backup approach to limiting permeability. However, liners have their own disadvantages. They can be difficult to fabricate and maintain, and they add weight to the pressure vessel. Their isotropic CTE usually cannot be matched to the anisotropic CTE of the composite thus, producing high stresses in the liner that promote cracking or debonding. In this effort two approaches to incorporating a barrier layer *directly into* a carbon / bismaleimide PMC (IM7 / 5250-4) were investigated for their effectiveness in preventing the development of damage networks that promote leakage. In the first concept, a "thin ply" of T800 carbon fiber / 5250-4 composite much thinner than a standard 0.13 mm thick ply was placed adjacent to the surface plies in one lay-up and next to the mid-plane ply group in a second lay-up. The surface plies and the mid-plane ply groups were known to develop transverse cracks prior to the other plies. It was also known from previous research that the cracks in these plies typically propagate into the adjacent plies as a series of short through-thickness "stitch cracks" centered on the parent crack.[7] It was hoped that the thin plies would stop or delay the formation of these stitch cracks. In the second concept, an even thinner layer (< 0.025 mm thick) of electro-spun PAN fibers infused with 5250-4 was again placed next to the surface plies. In previous work, IM6 / 3501-6 carbon / epoxy laminates with an electro-spun fiber layer inserted at several ply interfaces showed a tendency for reduced delamination from mechanical fatigue.[8] It was hoped that a similar reduction of delamination would be observed when thermal cycling was applied to the current materials. Each of the barrier ply composites was cryogenically cycled and the damage assessed for comparison with the damage in a baseline material with no barrier plies.

II. Experimental

A. Materials

Four materials were made. The first was the baseline material which consisted of IM7 medium modulus carbon fibers from Hexcel in a 5250-4 bismaleimide matrix from Cytec. The lay-up for this material was $[0/45/\text{-}45/90]_S$. The remaining three materials were a modification of the baseline material through the addition of barrier layers added with the goal of improving the micro-crack resistance and / or reducing the permeability due to thermal cycling while adding only a minimum amount of material to the laminate. Essentially, these materials had barrier plies fabricated as an integral part of the material rather than bonding a barrier material (liner) to one surface of the laminate. This approach was believed to be better than a liner since a liner is commonly attached to one surface (usually the interior) of a pressure vessel and often has significantly different mechanical and CTE properties than the base composite which can lead to eventual detachment of the liner.

The first two of the barrier ply materials incorporated thin plies of T800 / 5250-4. The fibers for the thin plies were provided by Think Composites under a Cooperative Research and Development Agreement with the Air Force. Think Composites obtained the unidirectional fiber layers in sheets held together with a binder. The fibers were produced at Fukui Lab in Japan. Fukui Lab used a recently developed technique for spreading fiber tows using streams of air to distribute the fiber tows into a thin layer without damaging the fibers (see fixture in Figure 1a). Recent research relying on this technique has studied the properties of laminates that consisted completely of plies with a thickness as low as 0.040 mm. Quasi-isotropic composites consisting of these thin plies have been shown to delay the onset of transverse cracking and delamination due to mechanical fatigue as can be seen in Figure 1b which is a comparison of x-rays of thick and thin ply open hole laminates made from the same constituents and loaded identically.[9-10] With this in mind laminates were fabricated for the current project by placing the spread tow (T800 fiber) between standard thickness plies of the IM7 / 5250-4 prepreg. During processing the thin layers of material became infused with the resin from the neighboring standard thickness prepreg. Laminates of two lay-ups were fabricated. The first was $[0/45/\text{-}45/0_T/90]_S$ and the second was $[0/90_T/45/\text{-}45/90]_S$. In each of these lay-up designations, "T" stands for "thin ply". The final laminate thickness of the two lay-ups that included the thin plies was 1.17 mm as compared to the baseline composite that was 1.08 mm thick. While the thin plies incorporated T800 fibers and the remaining plies incorporated IM7 fibers, the IM7 and T800 fibers have similar modulus and CTE so that the ply-level properties of the thin ply were likely similar (but not tested) to those of the standard plies.

The third of the barrier ply materials incorporated even thinner plies (<0.025 mm thick layers) of fibers electro-spun[11] from PAN into a random mat with no binder. The lay-up for this material was $[0/E/45/\text{-}45/90]_S$ where "E" stands for the electro-spun layer which has no orientation since it consists of a random mat. The final thickness of these laminates was 1.10 mm compared to 1.08 mm for the baseline materials. Upon microscopic examination, it was clear that the electro-spun fiber layer melted during the cure process. The melting may have occurred early during the cure cycle since the electro-spun material was not stabilized with a heat treatment prior to being fabricated into the composite. Therefore, it likely functioned only as a thin "resin rich" region on the interface

between the 0° and 45° plies. The motivation for investigating this material for a barrier ply is that recent work has shown that there can be an advantage to adding a layer such as this on the interface between plies to reduce the amount of delamination that occurs during mechanical testing.[8] As has been shown in past research achieving substantial permeability in a material relies not only on a network of transverse cracks but also on delaminations at the base of these transverse cracks.[12-13] The four materials described above were hand laid-up and autoclave cured according to the manufacturer's recommendations. The laminates had a single ply thickness of 0.13 to 0.14 mm except for the barrier plies. All of the samples were 50.8 by 50.8 mm squares and were cut with the 0° plies parallel to one side of the sample.

B. Cryogenic Cycling / Damage Measurement

The thermal cycling apparatus consisted of a frame and stepper motor actuation system that moved a wire mesh sample container between positions inside a dewar of LN_2 at -196 °C, in front of an ambient air fan, and inside an oven (Figure 2). A solenoid valve electrically controlled by a silicon transistor temperature sensor, maintained the LN_2 level in the dewar. A 46 cm tall custom-made 1000 W convection oven above the ambient air fan provided the elevated portion of the thermal cycle. The bottom of the oven contained a 16 cm circular opening for the sample container to pass through. As with the top of the LN_2 dewar, the bottom of the oven remained open during cycling. Based on measurements of temperature equilibration times in samples with an embedded thermocouple, a cycle of 2 minutes in the LN_2 followed by 5 minutes at RT and 5 minutes in the oven was used. The oven was set at 177 °C for all four materials which is below the maximum dry service temperature of 204 °C for 5250-4. Each sample was polished on perpendicular sides prior to cycling, and ply-level cracks were observed on the sample edges at 200X with an optical microscope after 0, 1, 5, 15, 30, 75, 125, 175, 250, and 325 cycles. Cracks were counted along the full length of each edge. Only transverse cracks that extended fully through the thickness of a ply (or nearly through the thickness) were counted. Crack densities were recorded on each side for all plies for which fiber ends (and thus transverse cracks) were visible. The crack densities from individual plies symmetric about the mid-plane (e.g., the two 0° plies) from four samples of each laminate were averaged. Additionally, the crack densities in the +45º and -45° plies were scaled by dividing the crack density by *sin* (45°).

III. Results

A. $[0/45/-45/90_T/0]_S$ Thin Ply Lay-up

Figure 3 shows a micrograph of a sample with the $[0/45/-45/0_T/90]_S$ lay-up. The micrograph shows that the thickness of the 0° thin ply varies along the length of the sample, however, it is clearly, at most one-fourth to one-third as thick as the adjacent -45° ply. Figures 4 and 5 show the ply-by-ply micro-crack densities as a function -196 °C to 177 °C combined cryogenic and elevated temperature cycling of the baseline material and the thin ply modified material, respectively. While the micro-crack density in the surface ply in each lay-up remained very similar throughout cycling, there is substantial difference between the inner-ply micro-crack densities in the two materials. In both materials plies 3 and 6 required the most cycles of any of the plies before cracking initiated. In the baseline material, plies 3 and 6 had no cracks through 175 cycles, 0.1 cracks / cm through 250 cycles, and a substantial amount of 0.70 cracks / cm by 325 cycles. On the other hand, plies 3 and 6 of the thin ply modified material had no cracks through 325 cycles. No cracks were able to propagate from the mid-plane 90° ply group through the thin ply and into the -45° ply as a stitch crack. Figure 6 illustrates this with an image that shows a crack in the 90° ply group extending to the thin ply interface but not beyond.

Additionally, when comparing Figure 4 to Figure 5 there are in general, fewer cracks in the other interior plies (90° and +45° plies) in the thin ply modified composite. While it may have been expected that putting a thin 0° ply next to the 90° ply group would slow down crack propagation into the adjacent -45° ply, the reduced number of 90° ply cracks and +45° ply cracks was more surprising. Adding a small amount of additional 0° material gave the laminate more 0° material to constrain the 90° plies. Consequently, it would be expected that there should have been *more* cracks in the 90° plies rather than fewer. On the other hand, the thin 0° ply may have somewhat shielded the 90° plies from the surface 0° plies which would have been trying to constrain them. At any rate, the thin ply worked even better than expected to not only reduce the number of plies that cracked but the overall crack density in the laminate. This should have a significant effect on the leak resistance (permeability) of this composite. Further cycling, followed by permeability testing is necessary to demonstrate this for sure.

B. $[0/90_T/45/-45/90]_S$ Thin Ply Lay-up

Figure 7 shows a micrograph of a sample of the $[0/90_T/45/-45/90]_S$ lay-up. Again, the thin ply can be seen to vary in thickness significantly. The micro-crack densities in Figure 4 for the baseline $[0/45/-45/90]_S$ material can

now be compared to the micro-crack densities as a function of cycles in Figure 8 for the this lay-up of the thin ply modified IM7 / 5250-4. Care should be taken when comparing the data in Figure 4 to Figure 8 because the scale in Figure 8 has been increased to accommodate the increased surface ply crack density. While there were more surface ply cracks in the thin ply lay-up (15.8 cracks / cm) relative to the baseline material (11.9 cracks / cm), this lay-up appears to be even better at preventing interior ply cracks. No cracks propagated past the surface ply and the thin ply into the +45° ply. Figure 9a illustrates this with a micrograph showing a surface ply crack stopped at the interface with the thin ply. Interestingly, cracks did form in the thin ply as shown in Figure 9b, but were apparently not loaded sufficiently to propagate further into the +45° ply. In fact, while the micro-crack density for the thin plies is not plotted in Figure 8, the thin ply crack densities were similar to those in the surface plies.

Also, surprisingly, after 325 cycles the 90° ply crack density (4.33 cracks / cm) in the baseline $[0/45/-45/90]_S$ material is over 5 times greater than the 90° ply crack density (0.84 cracks / cm) in the thin ply $[0/90_T/45/-45/90]_S$ material, and no cracks have propagated from the 90° ply group into the -45° plies while in the baseline material the -45° ply crack density is 0.70 cracks / cm after 325 cycles. Clearly, positioning the thin ply next to the surface ply rather than the mid-plane 90° plies lead to substantially better damage suppression. The reason for this can be hypothesized as follows. The addition of a jump in ply orientation of 90° degrees next to the severely cracked surface ply reduced propagation of stitch cracks into the +45° plies. The addition of thin plies oriented at 90° also increased the amount of 90° material available to constrain the 0° degree ply (resulting in increased 0° ply crack density) and reduced the ratio of 0° ply material to 90° ply material resulting in fewer 90° ply cracks which in turn reduced the amount of -45° ply cracks that propagated from the 90° ply group.

C. $[0/E/45/-45/90]_S$ Electro Spun Polymer Fiber Lay-up

Figure 10 shows a micrograph of the electro-spun fiber layer modified IM7 / 5250-4. The image shows that the layer of electro-spun fiber is up to 10 times thinner than the surface ply layer. Nearly all of the cracks that propagated through the surface plies continued on through the electro-spun fiber layer as is also shown in Figure 10. However, there was less delamination (than in the baseline material) at the location where the surface ply crack extended into the +45° ply. It was not clear whether the +45° ply crack extended width-wise beyond the edge of the laminate or not. Unlike in the baseline material where a crack in the +45° ply and a surface ply crack usually did not line up on the sample edge (because the +45° crack initiated away from the edge of the sample), in the electro-spun fiber layer modified material the surface ply cracks and the +45° cracks always lined up. The data in Figure 4 can be compared to the data in Figure 11 which shows the micro-crack density in the electro-spun material as a function of -196 °C to 177 °C cycles. This comparison indicates that the electro-spun layer modified material has fewer cracks in plies 3-6 with only 0.07 cracks / cm in plies 3 and 6 after 325 cycles compared to 0.70 cracks / cm in the same plies of the baseline material.

IV. Conclusions

The use of thin plies was studied as a way of reducing damage in a polymer matrix composite due to cryogenic cycling. Two lay-ups of IM7 / 5250-4 ($[0/45/-45/0_T/90]_S$ and $[0/90_T/45/-45/90]_S$) and a baseline lay-up of the IM7 / 5250-4 ($[0/45/-45/90]_S$) were thermally cycled between –196 °C and 177 °C and inspected for ply level cracks after various intervals of cycling. Both of the thin ply lay-ups were very effective in reducing the proliferation of cracks beyond layers of the composite that were particularly susceptible to crack formation. For example, after 325 cycles the $[0/90_T/45/-45/90]_S$ samples had no cracks continue from the 0° ply into the +45° ply while the baseline samples had 16% of the 0° ply cracks continue into the 45° plies. The disadvantage of having 33% more cracks in the 0° plies of the $[0/90_T/45/-45/90]_S$ samples and substantial damage in the thin plies was not a significant problem because the goal was to keep at least one ply un-cracked (or nearly un-cracked) so that complete paths for gas flow through the thickness of the laminate could not form. Further, the thin ply lay-ups had less damage in the inner plies (non-surface plies) with the $[0/90_T/45/-45/90]_S$ samples again performing best.

Similarly, the damage in samples of $[0/E/45/-45/90]_S$ IM7 / 5250-4 that included two 0.025 mm thick plies of electro-spun PAN fibers was compared to damage in samples of the baseline $[0/45/-45/90]_S$ IM7 / 5250-4 lay-up after each had been subject to –196 °C and 177 °C cycling. This material had no reduction in crack propagation from the 0° plies into 45° plies but, in fact, had nearly the same or slightly more cracks in the 45° ply (and the 0° plies) than in the baseline lay-up. However, the addition of the electro-spun fiber layer was effective at reducing the amount of damage further away from the 0° ply with half as many cracks in the 90° plies and one-tenth as many cracks in the –45° plies. The electro-spun fiber layer may be acting as a flexible interface that does not allow the 0° ply to constrain the 90° ply as much as in the baseline material. I.e., it has the ability to reduce stress transfer between plies but not the ability to stop a crack already impinging on the electro-spun layer from passing through.

These results are encouraging for a number of reasons. While production of a composite completely from thin plies can be difficult and / or expensive, the composites in this study consisted mostly of standard thickness plies. Fabrication of laminates such as these that required only two thin plies is more likely to be feasible in terms of cost and ease of lay-up. Also, in the thin ply lay-ups and the electro-spun lay-up the full complement of the plies in the baseline material were retained and it was necessary to increase the laminate weight only a minor amount with the addition of the barrier plies. The added leak resistance was obtained for a very small weight penalty. A total of roughly one-half of a ply was added to the thin ply lay-ups and less than one-eighth of a ply to the composite with the electro-spun layer. Finally, this apparent increased leakage resistance was obtained without a liner material. The barrier layers were incorporated within the layers of the laminate, contained the same matrix material as the other layers, and were consequently, co-cured with the base material likely significantly reducing the possibility of eventual debonding from the base material.

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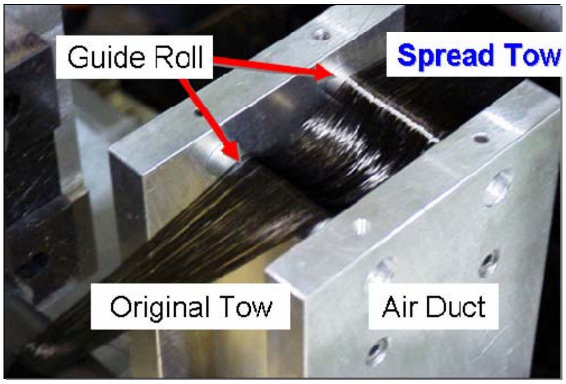

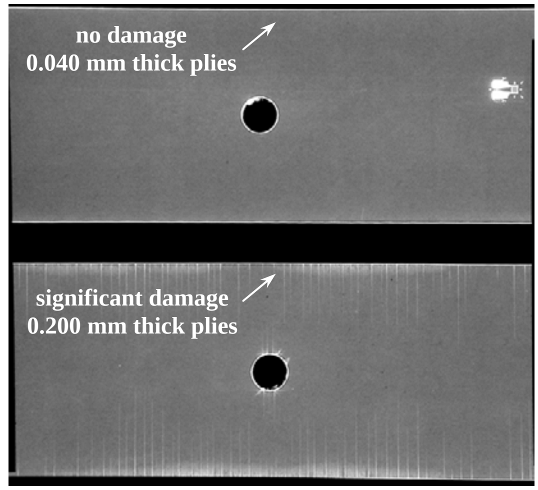

(a) **(b)**

Figure 1: Thin ply technology, (a) Fukui Lab's tow spreading device (b) X-rays of fatigued multi-angle composite laminates – thin ply composite versus standard ply composite[9]

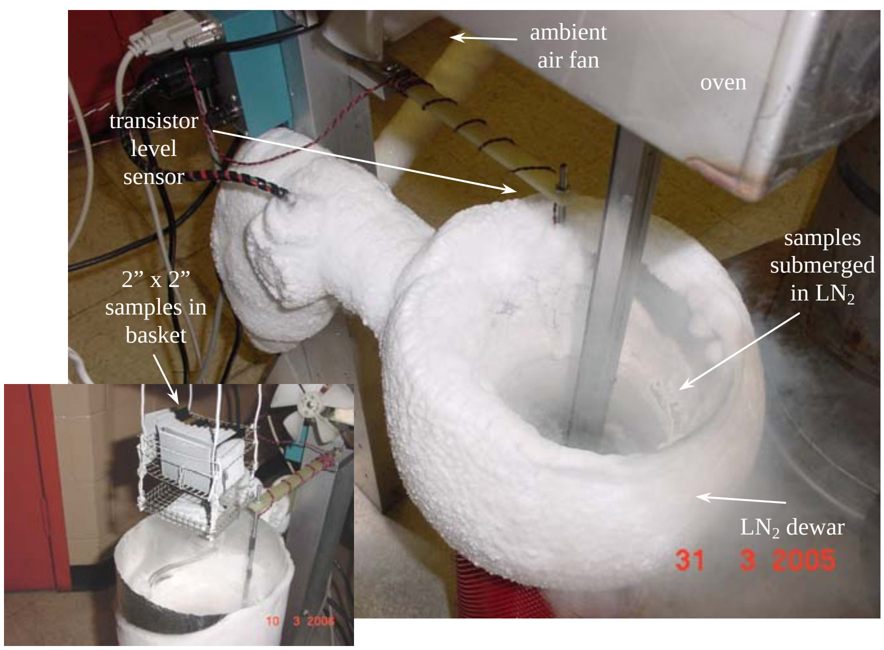

Figure 2: Cryogenic and elevated temperature thermal cycler

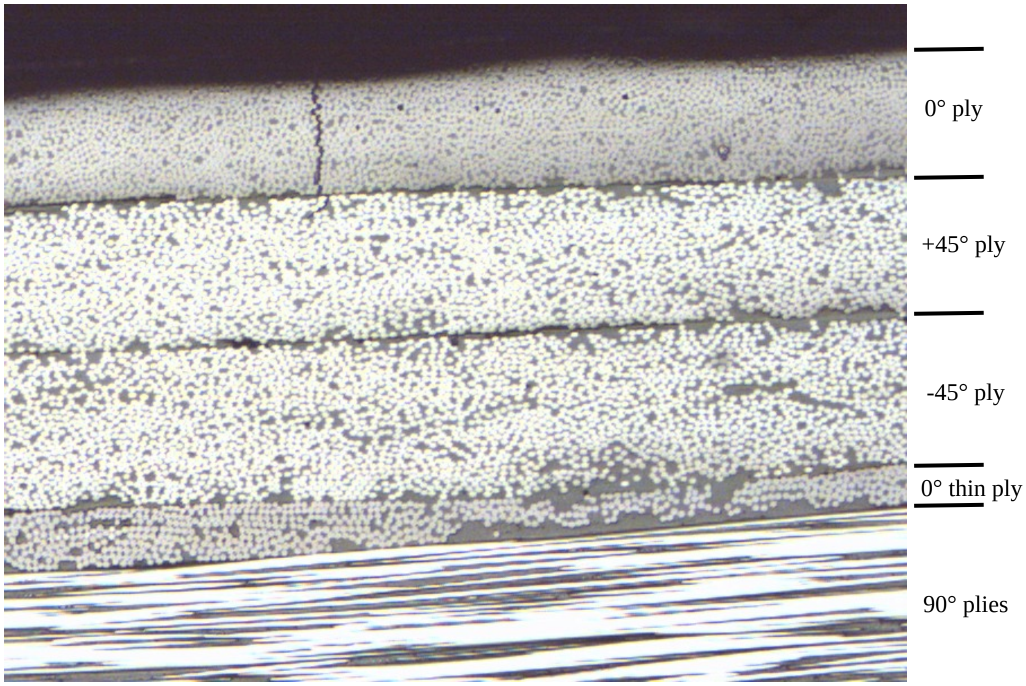

Figure 3: Image showing thin ply in IM7 / 5250-4 [0/45/-45/0_T/90]$_S$ lay-up

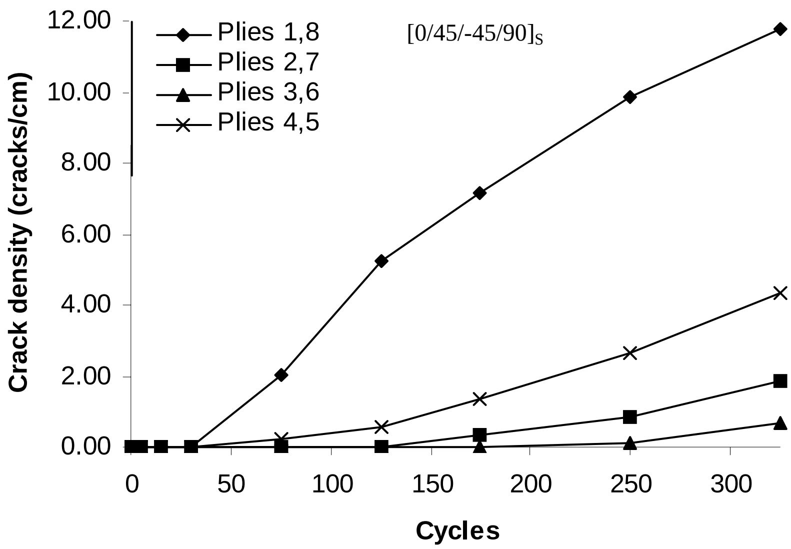

Figure 4: Micro-crack density versus -196 °C to 177 °C cycles in IM7 / 5250-4 [0/45/-45/90]$_S$ samples

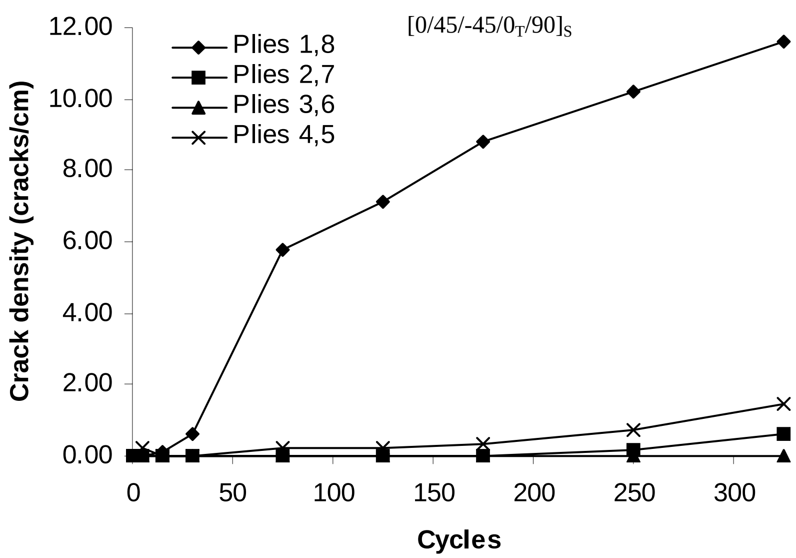

Figure 5: Micro-crack density versus -196 °C to 177 C cycles in IM7 / 5250-4 [0/45/-45/0$_T$/90]$_S$ samples

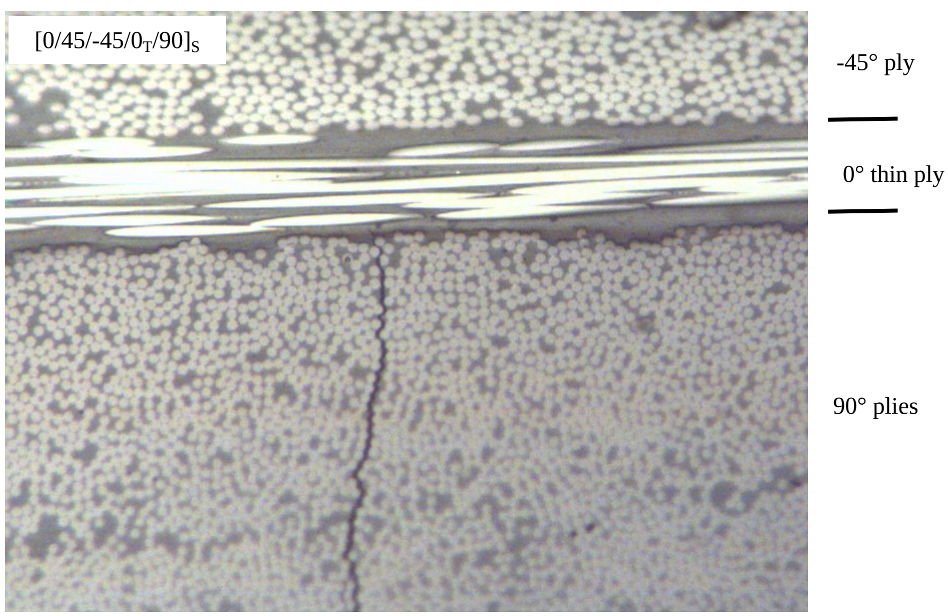

Figure 6: Crack in 90° ply group of [0/45/-45/0$_T$/90]$_S$ sample stopped at the interface with the thin ply

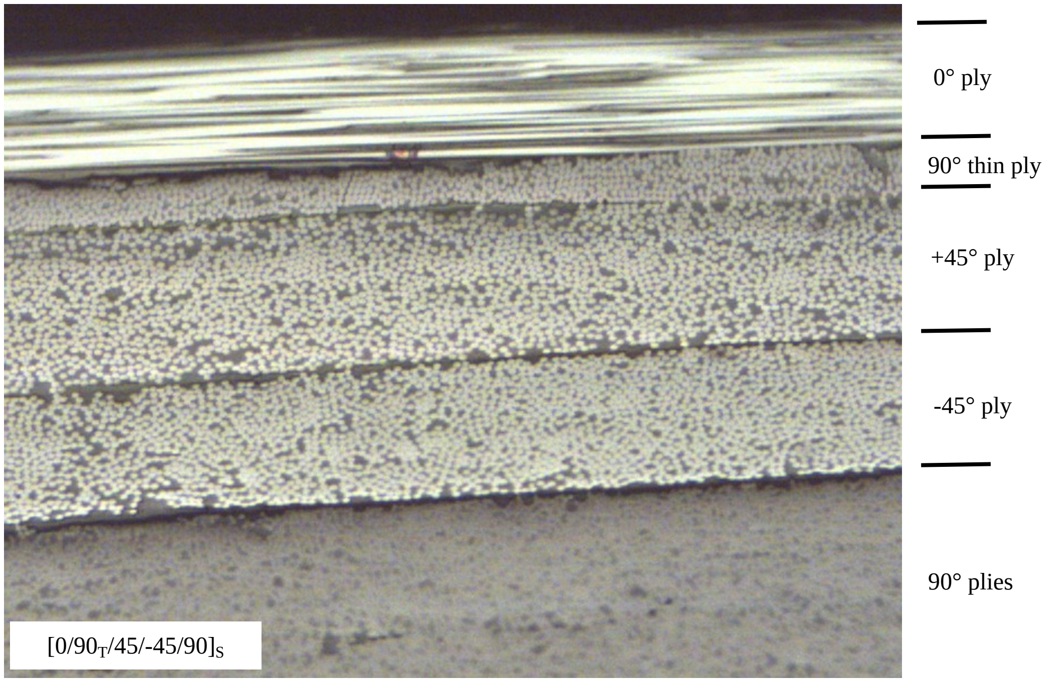

Figure 7: Image showing the location of the thin ply in a $[0/90_T/45/-45/90]_S$ sample

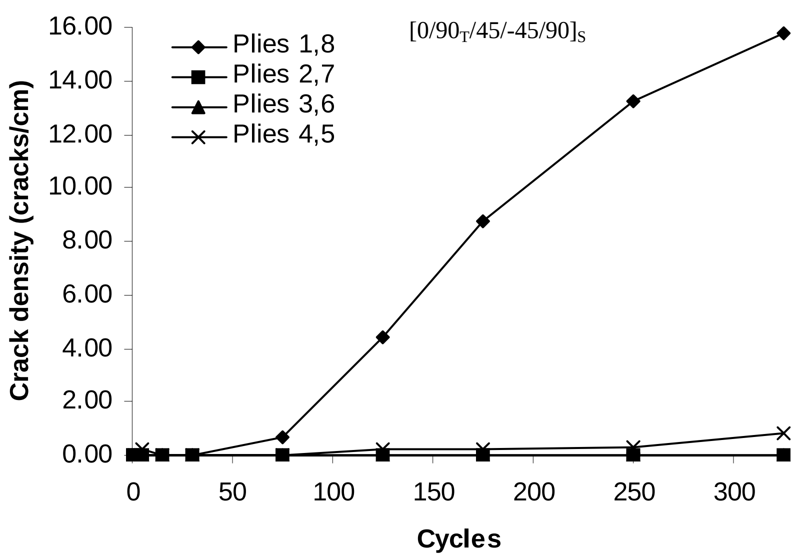

Figure 8: Micro-crack density versus -196 °C to 177 °C cycles in IM7 / 5250-4 $[0/90_T/45/-45/90]_S$ samples

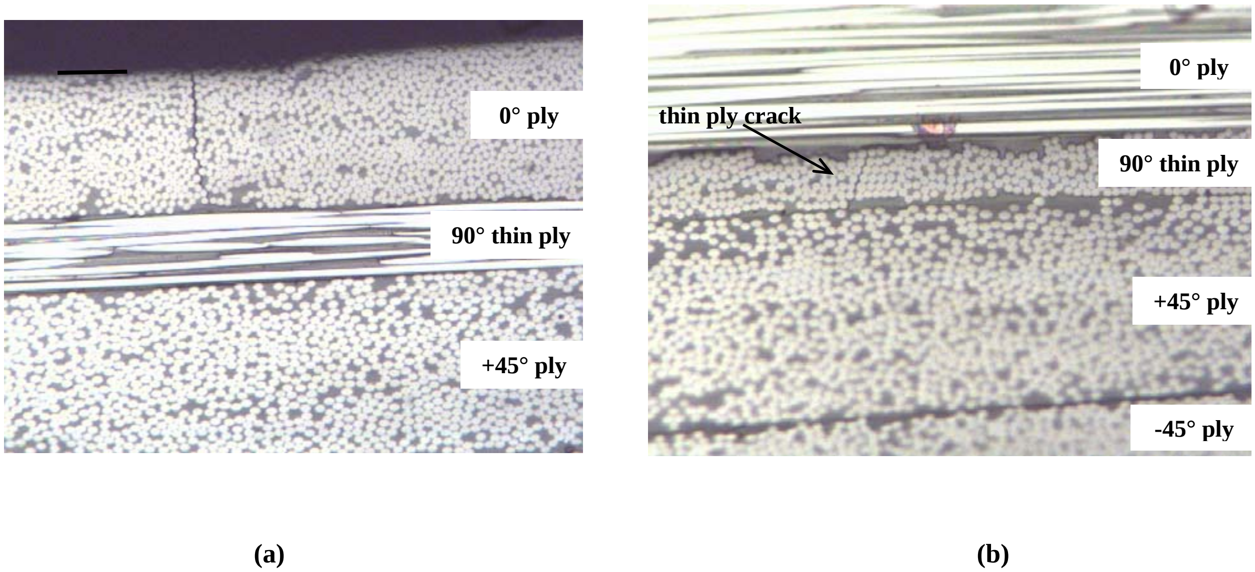

Figure 9: $[0/90_T/45/-45/90]_S$ a) surface ply crack stopped at interface with thin ply b) crack in thin ply

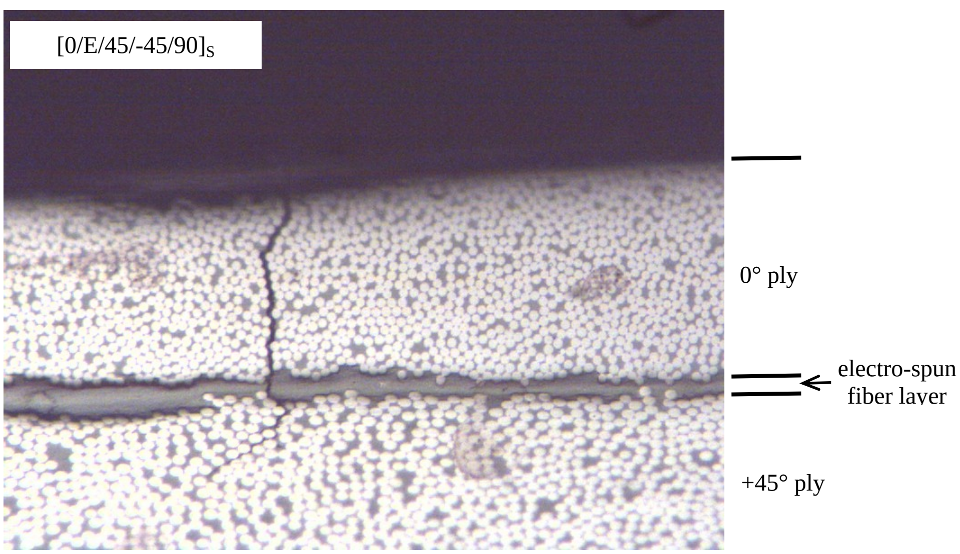

Figure 10: Image showing location of electro-spun fiber layer in $[0/E/45/-45/90]_S$ sample

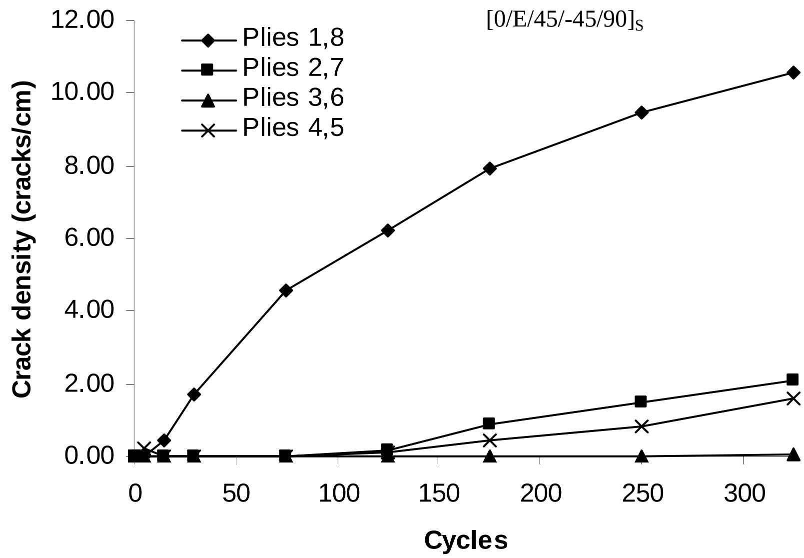

Figure 11: Micro-crack density versus -196 °C to 177 °C cycles in IM7 / 5250-4 [0/E/45/-45/90]$_S$ samples